Modeling Hydrochloric Acid Evaporation

in

ALOHA™

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INTRODUCTION

ALOHA is designed to model the release rate and dispersion of pure chemicals only; the property information in its chemical library is not valid for chemicals in solution or for mixtures of chemicals. However, solutions and mixtures are commonly manufactured and stored at chemical facilities or transported in large quantities. Emergency responders and planners often wish to predict how these chemicals would behave if accidentally released.

In some cases, it's possible to use ALOHA to model the behavior of a solution of hydrochloric acid. However, the method to do so is involved and time-consuming. To use it, you'll need some basic knowledge of physical chemistry. You'll also need to be aware of the potential pitfalls of the procedure. In this paper, we'll describe a method that you can use to estimate the evaporation rate of a 30% solution of hydrochloric acid, and we'll describe how you can use this rate estimate in ALOHA to obtain dispersion information. We'll also examine some basic information about chemical mixtures and solutions.

BACKGROUND

...About hydrochloric acid

Hydrochloric acid is a solution of hydrogen chloride (HCl) in water. While hydrogen chloride is included in ALOHA's chemical library (as either “hydrogen chloride” or “hydrochloric acid, anhydrous”), liquid hydrochloric acid is not. Because hydrogen chloride and hydrochloric acid behave very differently, it is not possible to use ALOHA's property values for hydrogen chloride in order to model hydrochloric acid. For example, the boiling point of hydrogen chloride, -85°C (-121°F), is well below ambient temperature, so it is a gas at ambient temperatures. ALOHA will expect it to escape from a tank directly into the atmosphere (without forming a puddle) as a two-phase, pressurized release. The boiling point of 30% hydrochloric acid, in contrast, is about 109°C (228°F), so it is a liquid at ambient temperatures. ALOHA will expect it to leak from a tank as a non-pressurized liquid, forming an evaporating puddle on the ground.

...About solutions and mixtures in general

It's difficult for a model like ALOHA to correctly predict the behavior of a solution or a mixture of chemicals because it's difficult to accurately predict chemical properties such as vapor pressure for solutions or mixtures. ALOHA's predictions of release rate and dispersion are greatly affected by this and other chemical properties. When an incorrect property value is used in ALOHA, the model's release rate and dispersion estimates will not be valid.

...About vapor pressure

Vapor pressure is the most important property determining evaporation rate of a liquid. A chemical in a solution or mixture will not display the same vapor pressure that it does when it's in pure form. An example is the vapor pressure of a mixture of ethanol and acetone. Pure ethanol (C_2H_6O) and pure acetone (C_3H_6O) have their own, individual vapor pressures at any given temperature. But the vapor pressure of either chemical will drop when it is mixed with the other. In the case of ideal mixtures[1] such as ethanol and acetone, the vapor pressures exerted by the component chemicals can easily be predicted using Raoult's Law (see example in Appendix A).

Deviations from Raoult's Law

A 30% solution of HCl in water is not an ideal mixture, because HCl is polar, and ionizes in water. For that reason, the partial pressure[2] of the HCl can't be accurately predicted using Raoult's Law. Instead, the most accurate value is an actual measurement of the partial pressure of HCl over an aqueous solution of HCl, at the ambient temperature and pressure of concern. Such a value can be found in a partial pressure table. Table 1 is a partial pressure table for HCl in aqueous solution at 1 atm pressure. These partial pressure data, for 10%, 20%, 30%, and 40% HCl solutions, are presented graphically in Figure 1.

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[1] A mixture of ethanol and acetone is called an “ideal mixture” because these two chemicals don’t interact strongly with each other when they’re mixed together.

[2] A chemical’s vapor pressure is called its partial pressure when the chemical exists in a mixture or solution.

Table 1. Partial pressures (in Pa) of HCl over aqueous HCl solutions.

%HCl	Temperature, °C 0	10	20	30	40	50	60	70	80	90	100
2		0.00156	0.00587	0.0201	0.0627	0.187	0.507	1.33	3.27	7.73	17.60
4	0.00240	0.00920	0.0320	0.103	0.307	0.853	2.20	5.40	12.7	28.0	61.3
6	0.00880	0.0312	0.101	0.300	0.827	2.17	5.33	12.5	27.5	58.66	123
8	0.0157	0.0777	0.237	0.687	1.81	4.59	10.8	24.4	52.0	109	219
10	0.0560	0.179	0.527	1.48	3.76	9.20	20.9	46.7	97.3	197	387
12	0.132	0.407	1.17	3.12	7.73	18.1	40.7	88.0	179	353	680
14	0.320	0.947	2.61	6.67	16.1	36.7	80.0	167	333	640	1200
16	0.747	2.13	5.71	14.1	32.9	73.3	156	320	621	1173	2146
18	1.80	4.93	12.7	30.4	68.7	148	307	607	1147	2093	3733
20	4.21	11.2	27.3	64.0	141	295	587	1133	2080	3746	6533
22	9.79	24.9	60.0	136	291	589	1147	2173	3906	6933	11999
24	23.3	57.3	133	289	600	1187	2253	4133	7266	12532	20932
26	54.7	131	289	608	1227	2333	4333	7799	13332	22531	36797
28	133	303	653	1320	2546	4760	8533	14932	25065	41196	65728
30	320	697	1413	2800	5253	9466	16532	27731	45329	72261	112657
32	760	1573	3133	5933	10799	18798	31731	51996	83060	129322	
34	1747	3520	6733	12266	21465	36397	59995	95992			
36	3866	7519	14065	25065	42930	71327	114657				
38	8399	15599	27998	47996	79727	127323					
40	17332	31064	53195	83593							
42	33730	57328	94525								
44	67994	111990									
46	125323										

Source: Chemical Safety Data Sheet SD-39. Properties and essential information for safe handling and use of hydrochloric acid, aqueous and hydrogen chloride, anhydrous. Manufacturing Chemists Association. Revised May 1970.

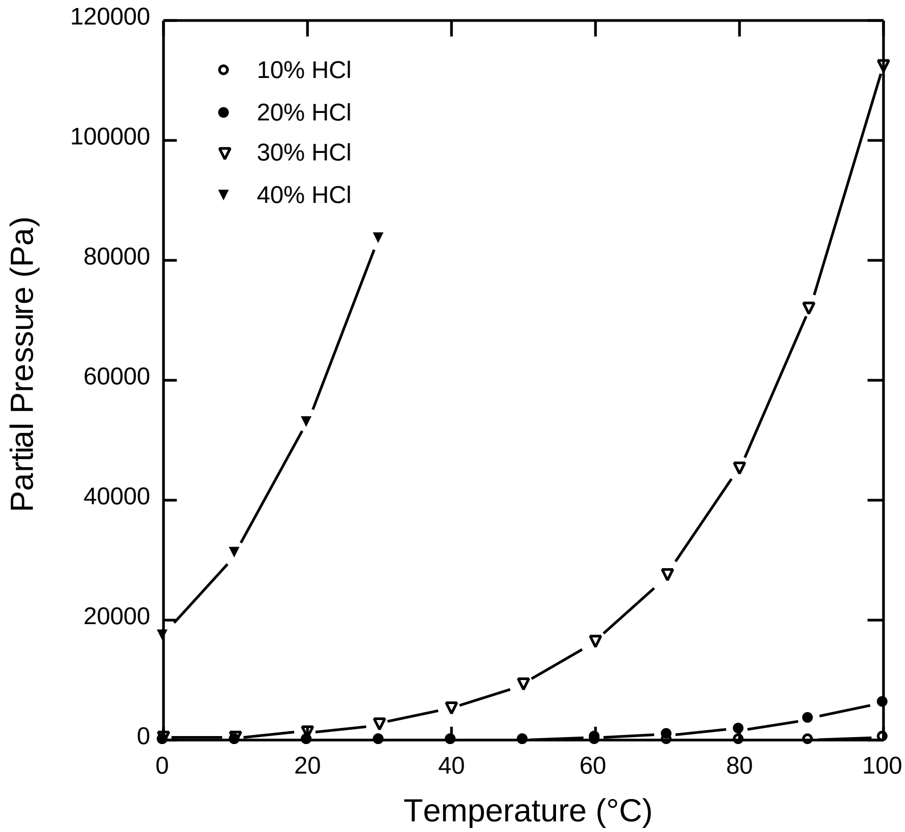


Figure 1. Partial pressures (in Pa) of HCl over aqueous 10%, 20%, 30%, and 40% HCl solutions.

MODELING HYDROCHLORIC ACID EVAPORATION: A METHOD

We'll follow a two-step procedure to model the evaporation and dispersion of 30% hydrochloric acid in ALOHA. This procedure is appropriate only for non-boiling, evaporating puddles (puddles at temperatures below boiling). First, we'll manually calculate a value for evaporation rate of the hydrochloric acid. We need to do this because we can't run ALOHA's Puddle model for a solution or mixture of chemicals (we have no way of providing accurate property information to the model). Second, we'll use this evaporation rate estimate as our estimate of source strength in ALOHA's Direct Source option. We'll then be able to obtain footprint and downwind concentration estimates from ALOHA.

A scenario description

We'll assume that ambient temperature is 20°C, that wind speed is 5 m/s, ground roughness is “Open Country,” and stability class is D. We'll assume complete cloud cover and 50% relative humidity. We'll also assume that our puddle of hydrochloric acid is circular, with a diameter of 10 m and an area of about 79 m^2.

Calculating evaporation rate

We can use the following equation[3] (Kawamura and Mackay 1985) to calculate evaporation rate.

$$E = A \times K_M \times \left(\frac{M_W \times P_V}{R \times T} \right) (\mathrm{kg\ s^{-1}}) \qquad \text{(Eq. 1)}$$

where E = evaporation rate, in kg s^{-1}

A = area of the evaporating puddle (79 m^2)

K_M = mass transfer coefficient, in m s^{-1}

M_W = molecular weight of HCl (36.5 kg $kmol^{-1}$)

P_V = vapor pressure, in Pa

R = the gas constant (8314 J $kmol^{-1}$ K^{-1}), and

T = ambient temperature, in K (20°C is equal to 293.2 K).

We'll calculate the evaporation rate of the 30% of the solution that is HCl. As an approximation, we're ignoring the evaporation of the 70% of the solution that is water, along with the water vapor already in the air, since water isn't a hazardous chemical. We'll therefore use the partial pressure of HCl over 30% hydrochloric acid at 20°C and 1 atm pressure as our estimate of vapor pressure. Table 1 shows that the partial pressure of HCl over a 30% hydrochloric acid solution at 20°C is 1,413 Pa.

The only one of the values in Equation 1 that we don't already know is K_M, the mass transfer coefficient. We can use the following equation (Mackay and Matsugu 1973) to calculate it:

$$K_M = 0.0048 \times U^{7/9} \times Z^{-1/9} \times S_C^{-2/3} (\mathrm{m\ s^{-1}}) \qquad \text{(Eq. 2)}$$

where K_M = mass transfer coefficient of the HCl, in m s^{-1}

U = wind speed at a height of 10 m (5 m s^{-1})

Z = the pool diameter in the along-wind direction (10 m), and

S_C = the laminar Schmidt number for HCl.

[3] This equation was used in all versions of ALOHA prior to 5.0. The current version of ALOHA uses a different method, formulated by Brighton (1985, 1990), that is too complex to use here.

The Schmidt number, which is a unitless ratio, can be calculated by:

$$Sc = \frac{v}{D_M} \qquad \text{(Eq. 3)}$$

where S_C = the laminar Schmidt number for HCl,
v = the kinematic viscosity of the air ($m^2\ s^{-1}$),
D_M = the molecular diffusivity of HCl in air ($m^2\ s^{-1}$)

We'll use ALOHA's value for v, $1.5 \times 10^{-5}\ m^2\ s^{-1}$. We'll also use its method of calculating D_M. ALOHA uses Graham's Law to approximate the molecular diffusivity of a chemical (Thibodeaux 1979) as:

$$D_M = D_{H_2O} \times \sqrt{\frac{Mw_{H_2O}}{Mw_m}}\ (\mathrm{m}^2\ \mathrm{s}^{-1}) \qquad \text{(Eq. 4)}$$

where D_M = the molecular diffusivity of HCl in air, in $m^2\ s^{-1}$,
D_{H2O} = the molecular diffusivity of water ($2.4 \times 10^{-5}\ m^2\ s^{-1}$ at 8°C),
$Mw_{\ H2O}$ = the molecular weight of water (18 kg $kmol^{-1}$), and
$Mw_{\ m}$ = the molecular weight of HCl (36.5 kg $kmol^{-1}$).

MODELING HYDROCHLORIC ACID EVAPORATION: AN EXAMPLE

We'll work backwards through Equations 1 to 4 to obtain our evaporation rate estimate for 30% hydrochloric acid.

Using Equation 4, we can estimate molecular diffusivity of HCl:

$$D_M = 2.4 \times 10^{-5} \times \sqrt{\frac{18}{36.5}} = 1.7 \times 10^{-5}\,\mathrm{m}^2\ \mathrm{s}^{-1}$$

Now we can use Equation 3 to estimate the Schmidt number for HCl:

$$Sc = \frac{1.5 \times 10^{-5}}{1.7 \times 10^{-5}} = 0.9$$

We can then use this value in Equation 2 to estimate the mass transfer coefficient for HCl:

$$K_M = 0.0048 \times 5^{7/9} \times 10^{-1/9} \times 0.9^{-2/3} = 0.014 \text{ m s}^{-1}$$

Finally, we can use Equation 1 to estimate the evaporation rate of the HCl:

$$E = 79 \times 0.014 \times \left(\frac{36.5 \times 1413}{8314 \times 293.2}\right) = 0.023 \text{ kg s}^{-1}$$

Two simplifications that we might have made

It's possible to simplify these calculations a little, although doing so may reduce the accuracy of your results.

First, Schmidt numbers typically range from 1 to 2.5 (Kawamura and Mackay 1985; Thibodeaux 1979). Using the smallest value in this range, 1, as the Schmidt number to calculate K_M, the mass transfer coefficient, usually will be a conservative approximation. That is, it will more likely to lead to an overestimate than an underestimate of K_M and hence evaporation rate. Note, though, that it may be a slightly non-conservative approximation in the case of hydrochloric acid (since we estimated Schmidt number to be 0.9 when we did not make this simplification).

Second, Mackay *et al.* (1980) suggest further simplifying the calculation of K_M by setting the puddle diameter term, $Z^{-1/9}$, equal to 1, since the power on Z is very small. As long as the puddle's along-wind diameter is at least 1 m, this is also a conservative approximation.

If we had used both of these simplifications, we would have calculated the mass transfer coefficient as:

$$K_M = 0.0048 \times U^{7/9} (\text{m s}^{-1})$$

We would have obtained a value for K_M of about 0.017 m s^{-1} and an estimated evaporation rate of about 0.028 kg s^{-1}, a value about 20% larger than the one that we obtained when we didn't make the simplifications.

A correction term for volatile chemicals

A volatile chemical is one that has a relatively high vapor pressure at environmental temperatures, and therefore evaporates readily. A 30% hydrochloric acid solution at 20°C is not very volatile; a 40% hydrochloric acid solution at the same temperature is much more volatile. If you use the method above to estimate evaporation rate of a volatile solution, you may wish to include the following correction term (Brighton 1985, 1990; Reynolds unpublished) in the evaporation equation, as shown below. This correction method is appropriate only for a chemical at a temperature below its boiling point.

First, calculate the correction term:

$$C = -\left(\frac{Pa}{Pv}\right)\ln\left(1 - \frac{Pv}{Pa}\right) \qquad \text{(Eq. 5)}$$

where Pa = atmospheric pressure, in Pa (101,325 Pa at sea level), and
Pv = vapor pressure of the component of concern, in Pa.

For chemicals that are not very volatile, the value of C will be about 1.0. It will increase in magnitude as the vapor pressure of the chemical increases.

Then calculate the corrected evaporation rate as

$$E_c = C \times E \text{ (kg s}^{-1}\text{)} \qquad \text{(Eq. 5)}$$

where E_c = evaporation rate corrected for volatility.

In the case of 30% hydrochloric acid at 20°C, this correction makes very little difference:

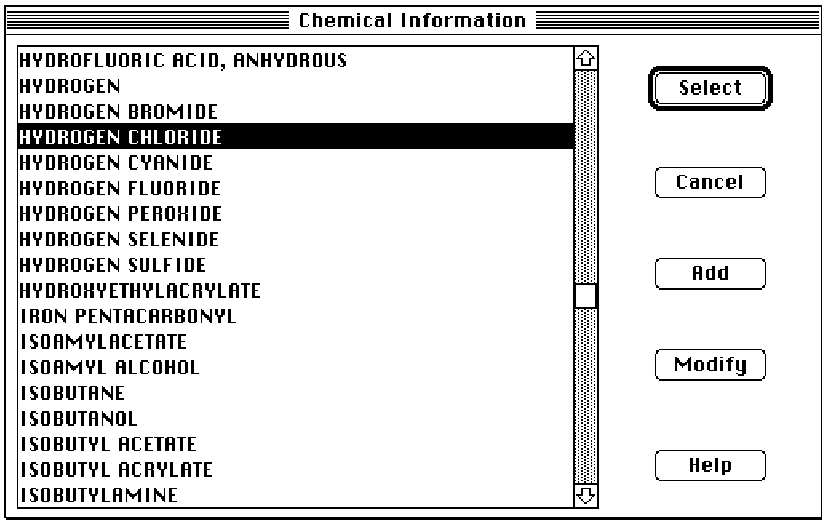
$$C = -\left(\frac{101325}{1413}\right)\ln\left(1 - \frac{1413}{101325}\right) = 1.007$$

and

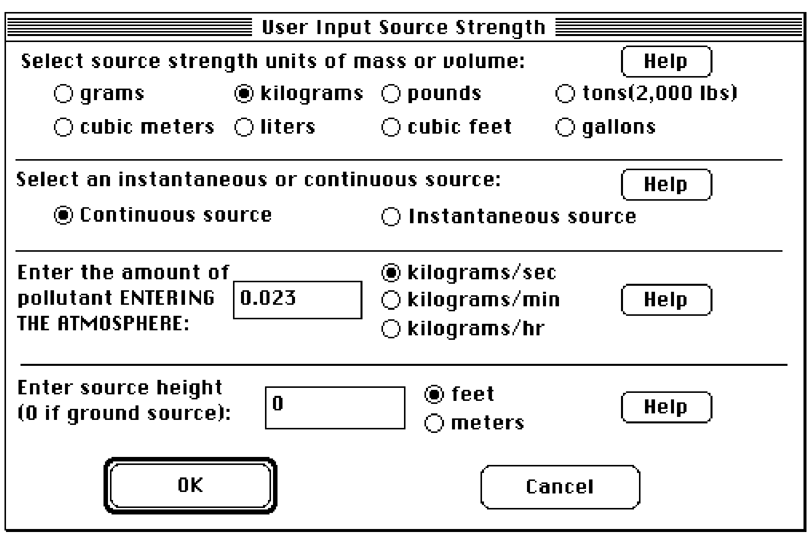
$$E_c = 1.007 \times 0.023 \text{ kg s}^{-1} = 0.023 \text{ kg s}^{-1}$$

Using the evaporation estimate in ALOHA

Here's how to use this evaporation rate estimate in ALOHA. Once you have opened ALOHA and chosen a spill location, choose **Chemical...** from ALOHA's **SetUp** menu. The evaporation rate estimate that we've obtained above is for the hydrogen chloride component in a 30% solution of hydrochloric acid. So find “HYDROGEN CHLORIDE,” click on this name to highlight it, then click **Select**.

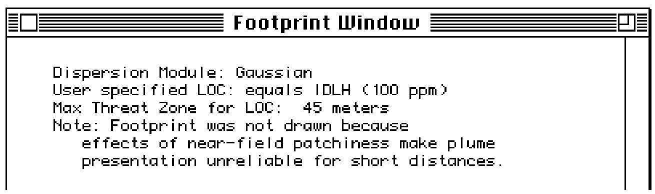


Enter the meteorological information for the scenario by choosing **Atmospheric**, then **User Input...** from the **SetUp** menu. Once you've done so, it's possible to choose **Direct...** from the **Source** submenu under the **SetUp** menu. Enter the estimated evaporation rate as a continuous source strength, as in the example screen below.

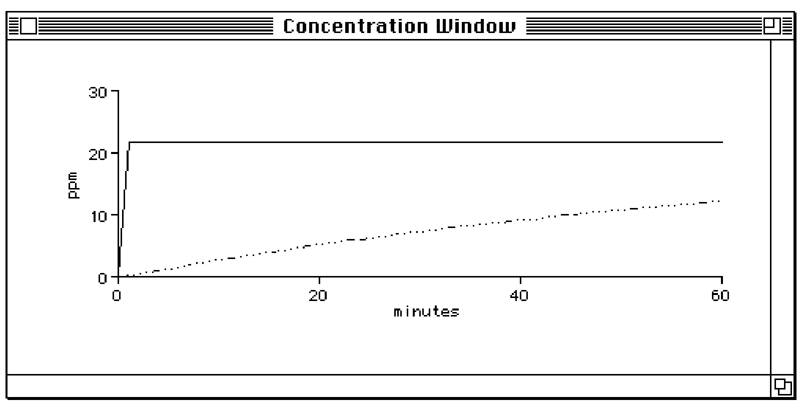


Before ALOHA can produce a footprint graph, you'll need to select a level of concern. The IDLH of hydrogen chloride, 100 ppm, may be an appropriate value to use (you may wish to use a different toxic threshold). Enter your value into ALOHA by choosing **Options...** from the **Display** menu.

Choose **Footprint** from the **Display** menu to prompt ALOHA to make footprint calculations. For this scenario, it calculates a downwind distance of 45 m. Because ALOHA cannot account for the effects of concentration patchiness this close to the point of release, it does not draw a footprint.



However, it can produce concentration and dose graphs for locations that you specify (choose **Concentration...** from the **Display** menu to indicate a location). For a location 100 m downwind and along the plume centerline, for example, ALOHA predicts that outdoor concentrations will reach about 22 ppm.



ADDITIONAL POINTS

If you choose to model a solution of hydrochloric acid in ALOHA, first consider the following points:

- Even if you carefully follow the method above, or a similar method, ALOHA's results are likely to be less accurate than if you were modeling evaporation and dispersion of pure hydrogen chloride. This is because you must use a constant evaporation rate as your estimate of source strength. In reality, evaporation rate of a puddle usually changes over time, as puddle temperature rises or falls, and as its radius changes. In effect, you must instead tell ALOHA that evaporation rate will remain constant, because you have no way to predict how the rate may change over time.

- This method for estimating evaporation rate is appropriate for non-boiling puddles only. A puddle is non-boiling when its boiling point is above ambient temperature.

- Remember that you should use Raoult's Law to estimate a solution component's partial pressure only if you know that the components of the solution don't interact. Otherwise, be sure to use a partial pressure value from a partial pressure table, or a partial pressure value that you have measured.

- To make its evaporation calculations, ALOHA mathematically treats a puddle as a point source. This means that its results are least accurate when a puddle is very large and the location for which you'd like to produce a concentration graph is very close to the puddle. Consider using another method or model in such a case.

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APPENDIX

Raoult's Law states that the partial pressure of any single component in an ideal mixture is the product of (a) its vapor pressure when it's in pure form at the same temperature and pressure and (b) the mole fraction[4] of that component within the mixture. That is,

$$P_i = V_i \times x_i \tag{Eq. 7}$$

where P_i is the partial pressure of the component, V_i is its vapor pressure when it's in pure form, and x_i is the mole fraction of the component in the mixture.

As an example, consider a mixture containing 25% by weight of acetone and 75% by weight of ethanol. The partial pressures of ethanol and acetone in this mixture at 20°C can be calculated as follows:

First, obtain vapor pressure values for both components. The vapor pressure of pure ethanol at 20°C and 1 atm pressure is 5,887 Pa; the vapor pressure of acetone under the same conditions is 24,585 Pa (Daubert and Danner 1989).

Second, calculate the mole fraction of each component. The molecular weights of acetone and ethanol are 58 g / mol and 46 g / mol, respectively. In 100 g of the mixture, there are 25 g acetone and 75 g ethanol. Calculate the number of moles of each component within the mixture:

$$\frac{25\text{ g}}{58\text{ g / mol}} = 0.43\text{ mol acetone} \quad \text{and} \quad \frac{75\text{ g}}{46\text{ g / mol}} = 1.63\text{ mol ethanol}$$

Third, calculate the mole fraction of each component as the ratio of the number of moles of that component and the total number of moles in the 100 g of the mixture:

$$\frac{0.43\text{ mol}}{(1.63\text{ mol} + 0.43\text{ mol})} = 0.21\text{ mole fraction acetone}$$

$$\frac{1.63\text{ mol}}{(1.63\text{ mol} + 0.43\text{ mol})} = 0.79\text{ mole fraction ethanol}$$

[4] The mole fraction of a chemical within a mixture is the fraction of all the molecules in the mixture that are molecules of that chemical. Values for mole fraction vary between 0 and 1. A chemical's mole fraction is equal to its concentration in ppm, divided by 1,000,000.

Finally, calculate the partial pressure of each component:

Partial pressure of ethanol = 5,887 Pa × 0.79 = 4,651 Pa
Partial pressure of acetone = 24,585 Pa × 0.21 = 5,183 Pa